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Numerical Study on the Ignition Process of *n*-Decane/Toluene Binary Fuel Blends

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ABSTRACT: Fuel blends are widely utilized in high-performance combustion engines and surrogate fuel models. It is essential to understand thoroughly the fundamental combustion properties such as the ignition delay time, laminar flame speed, and extinction strain rate of fuel blends. In this study, the unsteady ignition process of *n*-decane/toluene binary fuel blends is investigated numerically with detailed reaction mechanism and transport properties. The emphasis is spent on assessing the kinetic and transport effects of toluene addition on the premixed and nonpremixed ignition of *n*-decane with air. Two configurations are considered: a static premixed homogeneous configuration to examine the chemical kinetics and a nonpremixed counterflow configuration to assess the effects of kinetics as well as transport. For the homogeneous ignition process, the ignition delay time is found to be strongly affected by the toluene molar fraction in the binary fuel blends. Sensitivity analysis and reaction path analysis are conducted and key elementary reactions involved in the ignition inhibition by toluene addition are identified. For the nonpremixed ignition process, the ignition delay time is shown to be strongly affected by the strain rate as well as the toluene blending ratio. The transport effects on the nonpremixed ignition process are examined with the help of scalar dissipation rate and sensitivity analysis. It is demonstrated that the diffusion transport plays a very important role in the nonpremixed ignition process.

1. INTRODUCTION

Binary fuel blends are widely utilized in developing highefficiency and low-emission internal combustion engines.¹ For examples, gasoline/ethanol,² diesel/ethanol,³ and diesel/oxygenated additives⁴ can reduce the engine emission and partly realize the substitution of gasoline or diesel. Fuel blending is also an effective way to control the ignition in Homogeneous Charge Compression Ignition (HCCI) engines, in which the octane number of fuel blends such as *n*-heptane/iso-octane,⁵ *n*-heptane/ alcohol,⁶ and *n*-butane/DME⁷ can be adjusted to meet the requirements for stable engine operation at different conditions. Since the fundamental combustion properties such as the ignition delay time, laminar flame speed, and extinction strain rate play an important role in combustion engines, it is essential to understand thoroughly these properties of fuel blends.⁸⁻¹² In the literature, there are extensive studies on the fundamental combustion properties of single fuel component. However, research on fuel blends is deficit compared with their application in practical combustors. Due to the strong nonlinearity in chemical reactions, the burning properties of fuel blends cannot be obtained from linear combination of properties of each individual fuel component.¹³ Therefore, experiments and numerical simulations should be conducted to understand the fundamental combustion properties of fuel blends.

Furthermore, understanding fundamental combustion properties of fuel blends is crucial for developing reliable surrogate fuel models.^{14–16} By choosing proper representative fuel components and adjusting their ratios, one can match the combustion and emission properties of practical fuels using surrogate models. For example, as one of the most common practical fuels used for transportation, gasoline usually contains hundreds of species including alkanes, cycloalkanes, aromatics, sulfides, and oxygen compounds. That poses a great challenge for the study of its combustion properties by numerical simulation with detailed chemical mechanisms. However, the ignition delay time and laminar flame speed of gasoline can now be reproduced using the Primary Reference Fuels (PRF) model.^{17–19} Unfortunately, the ratio of hydrogen to carbon (H/C ratio) of gasoline cannot be accurately reproduced by the PRF model. Recently, adding aromatics into alkanes has received some attention, 19-22 since it can simultaneously reproduce the H/C ratio and other combustion properties of practical fuels. Due to the difference in chemical structure and molecular weight, aromatic fuel addition into alkanes greatly affects the chemical kinetics as well as transport in the combustion process.²³⁻²⁵ Therefore, it is essential to understand the combustion properties of alkanes with aromatics addition.

In the present work, *n*-decane and toluene are chosen as representatives of alkanes and aromatics, respectively. *n*-Decane has large molecular weight and is a proper representative of alkanes in jet fuel.¹⁴ Toluene is one of the simplest alkyl aromatic fuels. Moreover, the high-temperature oxidation mechanism of *n*-decane and toluene has been well developed.^{26,27} Recently, the extinction limits of *n*-decane/toluene diffusion flames have been studied.^{20,21} Humer et al.²⁰ compared the extinction and autoignition characteristics of *n*-decane/toluene surrogates with those of jet fuels (JP-8 and Jet-A) and found that the critical extinction and autoignition conditions of the considered

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surrogates are slightly different from those of jet fuels. Won et al.²¹ found that toluene addition can significantly reduce the extinction strain rate of *n*-decane/air diffusion flame. However, there are no systematic studies on the ignition process of ndecane/toluene binary fuel blends in the literature. Therefore, the objective of this study is to assess and interpret the influence of toluene blending on the unsteady ignition of *n*-decane/air. We first investigate the homogeneous ignition process of *n*-decane/ toluene/air mixtures so that the kinetic effects of toluene addition can be assessed. The homogeneous ignition process does not have mass or heat transport and thereby is purely controlled by chemical kinetics. However, in practical combustion processes, the ignition is also affected by mixing of fuel and air as well as heat conduction.^{28–30} To understand the effects of kinetics and transport on the ignition of n-decane/ toluene binary fuel blends, we also study the nonpremixed ignition process.

2. NUMERICAL METHODS AND SPECIFICATIONS

The effects of toluene blending on the ignition of *n*-decane are investigated numerically using a homogeneous static configuration to examine the kinetic effects and a nonpremixed counterflow configuration to assess the effects of transport as well as its coupling with kinetics. The detailed mechanism for *n*-decane and toluene oxidation at high temperature is employed in simulation. This mechanism was developed by Chaos et al.,^{26,27} and it consists of 121 species and 866 elementary reactions. It was demonstrated that this mechanism can accurately predict the ignition of *n*-decane/air and toluene/air mixtures.^{26,27}

For the adiabatic homogeneous ignition process at constant pressure, the governing equations for the temperature, T, and the mass fraction of the kth species, Y_k are

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\sum_{k=1}^{N} (h_k \omega_k W_k)}{\rho C_\mathrm{p}} \tag{1}$$

$$\frac{\mathrm{d}Y_k}{\mathrm{d}t} = \frac{\omega_k W_k}{\rho} \text{ for } k = 1, 2, ..., N$$
(2)

where t, ρ , $C_{\rm p}$, ω_k , W_k , and N denote, respectively, the time, density, specific heat at constant pressure, production rate and molecular weight of the $k^{\rm th}$ species, and the total number of species. The chemical reaction rates and thermal properties at different conditions (temperature, pressure, and composition) are evaluated using the CHEMKIN package.³¹ The ordinary differential eqs 1 and 2 are integrated implicitly using the VODE solver.^{32,33} Numerical simulations are conducted for stoichiometric *n*-decane/toluene/air mixtures with the blending ratio (defined as the molar fraction of toluene in the binary fuel blends), *c*, ranging from zero (pure *n*-decane) to unity (pure toluene).

To assess the transport effects on the ignition of *n*-decane/ toluene binary fuel blends, the nonpremixed ignition process in a counterflow configuration is simulated using the code for unsteady counterflow flame described by Ju et al.³⁴ Details on the theoretical model and governing equations can be found in ref 34. The counter-flowing fuel jet is at 500 K, and it consists of toluene, *n*-decane, and nitrogen with the molar ratio of $C_7H_8/$ $C_{10}H_{22}/N_2 = c/(1 - c)/9$, and the hot air jet is at 1400 K. The pressure is fixed to be P = 1 atm. In the simulation, the initial temperature and species distributions are determined under a frozen flow constraint with all the reaction terms suppressed.³⁵ At time zero, the chemical reactions are allowed in the precalculated frozen flow field and the afterward evolution of the reactive counterflow system is simulated. The mixtureaverage diffusion model is employed in simulation. Similar procedures were used in previous studies by Chen et al.³⁵ and Liu et al.³⁶ The potential counterflow is considered, and thereby, the strain rate, *a*, is kept constant in the transient numerical simulation. The separation distance from the two inlet boundaries is 10 cm. To examine the transport effects on nonpremixed ignition, ignition processes at different toluene blending ratios and different strain rates are investigated.

3. RESULTS AND DISCUSSION

3.1. Homogeneous Ignition Process. There are many different ways to define the ignition delay time of the homogeneous ignition process. Two definitions are used here: one is the time when the temperature exceeds its initial value by 400 K (i.e., $\Delta T = 400$ K) and the other is the time when the largest heat release rate occurs (i.e., $Q = Q_{max}$). Figure 1 shows the



Figure 1. Change of the ignition delay time τ with the toluene blending ratio *c* for homogeneous stoichiometric *n*-decane/toluene/air mixture at $T_0 = 1400$ K and P = 1 atm.

ignition delay time, τ , as a function of toluene blending ratio *c* for stoichiometric *n*-decane/toluene/air mixtures at $T_0 = 1400$ K and atmospheric pressure. It is seen that the ignition delay times defined in these two methods are almost the same (the relative difference is within 2%). Therefore, in the remainder of this article only the definition based on temperature increase is used unless otherwise specified. Figure 1 demonstrates that the ignition delay time τ increases monotonically with the toluene blending ratio c. Two regimes are observed: in the first regime with $c \leq 0.6$, τ is insensitive to the change of *c* and the toluene addition has little effect on the ignition process; in the second regime with the toluene dilution ratio above a certain value (say, c > 0.6), τ increases exponentially with *c*. It is noted that the choice of c = 0.6 is somehow arbitrary, since there exists a transition region between the two regimes. In addition, we also employ another submechanism for toluene oxidation developed by Wang et al.³⁷ to test the validity of the present mechanism. Similar results to those shown in Figure 1 are obtained, and two distinct regimes of toluene addition discussed above are also observed.

The strongly nonlinear change of the ignition delay time τ with the blending ratio *c* is also observed for *n*-decane/toluene/air mixtures at other equivalence ratios, initial temperatures, and pressures. Figure 2 shows the change of the ignition delay time with the initial temperature at three different values of toluene blending ratio. Similarly to Figure 1, Figure 2 indicates that the



Figure 2. Ignition delay time as a function of the initial temperature for homogeneous stoichiometric *n*-decane/toluene/air mixture at atmospheric pressure.

ignition delay time is insensitive to toluene addition when $c \le 0.6$ and that the ignition delay time increases mainly in the regime of $0.6 < c \le 1.0$.

To understand the kinetics involved in the ignition inhibition and to explain the nonlinear change of the homogeneous ignition delay time with the toluene blending ratio, sensitivity analysis and reaction path analysis are conducted for the homogeneous ignition process. Figure 3 shows the temporal development of the radical pool (which is sum of the molar fractions of CH₃, H, O, OH, and HO₂) and H radical at various levels of toluene blending. It is noted that each of the five radicals (CH₃, H, O,



Figure 3. Temporal development of (a) the radical pool (sum of CH₃, H, O, OH, and HO₂) and (b) H radical during the homogeneous ignition of stoichiometric *n*-decane/toluene/air mixtures with different toluene blending ratios ($T_0 = 1400$ K, P = 1 atm).

OH, and HO_2) considered here plays different role in fuel oxidation and has its own distinctive evolution pattern. However, the effects of toluene addition on them are very similar to each other and to that on the radical pool shown in Figure 3a. It is seen in Figure 3 that toluene addition inhibits the development of the radical pool. This inhibition effect is shown to increase with the toluene blending ratio, which results in the nonlinear ignition-inhibition behavior observed in Figure 1. Furthermore, the radical molar fraction is shown to decrease greatly with the toluene blending ratio.

The inhibitive effect of toluene addition on the radical build-up demonstrated in Figure 3 is purely caused by chemical kinetics. To identify the main elementary reactions involved in the ignition inhibition, sensitivity analysis is conducted. The sensitivity coefficient of the ignition delay time with respect to the reaction rate of the i^{th} elementary reaction is calculated according to the following expression:

$$S_{i} = 10 \frac{\tau(1.1k_{i}) - \tau(k_{i})}{\tau(k_{i})}$$
(3)

where $\tau_i(1.1k_i)$ represents the ignition delay time when the rate constant of the *i*th elementary reaction is artificially modified to be 1.1 times of its original value (k_i) . A negative (positive) value of S_i indicates that the ignition process is promoted (inhibited) by the *i*th elementary reaction. The results from sensitivity analysis at different blending ratios are presented in Figure 4. When toluene



Figure 4. Sensitivity coefficients of the homogeneous ignition delay time of stoichiometric *n*-decane/toluene/air mixtures with respect to the reaction rates of elementary reactions ($T_0 = 1400$ K, P = 1 atm).

is added, H and OH radicals react with toluene through reactions $C_6H_5CH_3 + H = C_6H_5CH_2+H_2$ (R767) and $C_6H_5CH_3 + OH = C_6H_5CH_2 + H_2O$ (R769). These two reactions replace H and OH radicals with $C_6H_5CH_2$ radical, which is a rather stable one, and thereby lengthen the radical pool buildup and slow down the ignition process. Therefore, positive sensitivity coefficients for these two elementary reactions are shown in Figure 4. Moreover, it is observed that the sensitivity coefficients for these two elementary reactions change nonmonotonically with the toluene blending ratio *c*. This is due to the fact that when the blending ratio is close to unity, the molar fractions of H and OH radicals drop greatly during the development of the radical pool as indicated in Figure 3.

Since the ignition inhibition by toluene addition is due to the fact that H and OH radicals are consumed through reactions R767 and R769, reaction path analysis for H and OH radicals are conducted. The contribution of the i^{th} reaction to the



Figure 5. Contribution of dominant reactions to the production/consumption of H and OH radicals during the homogeneous ignition of stoichiometric *n*-decane/toluene/air mixtures: (a) c = 0.0, (b) c = 0.75, and (c) c = 1.0 for H production/consumption; and (d) c = 0.0, (e) c = 0.75, and (f) c = 1.0 for OH production/consumption ($T_0 = 1400$ K, P = 1 atm).

concentration change of a certain intermediate species is defined as^{38}

$$C_{i} = f_{i} / \sum_{i=1}^{M} (|f_{i}|)$$
(4)

where f_i represents the rate of change in the concentration of the considered species due to the *i*th reaction, and *M* is the total number of elementary reactions. The positive (negative) value of C_i indicates that the considered species is generated (consumed) by the *i*th reaction. The results at three different blending ratios (c = 0, 0.75, and 1.0) are presented in Figure 5, in which the elementary reactions involved are listed in Table 1. It is seen that, with the increase of toluene blending, reactions R767 and R769 become more important in the consumption of H and OH radicals, respectively. Besides, the OH consumption rate through reaction R769 is shown to be always larger than the OH production rate through the reaction $C_6H_5CH_2 + HO_2 =$

Table 1. List of Reactions Presented in Figures 5 and 11

no.	reaction
R1	$H + O_2 = O + OH$
R29	$CO + OH = CO_2 + H$
R44	$CH_2O + OH = HCO + H_2O$
R50	$CH_3 + O_2 = CH_2O + OH$
R51	$CH_3 + HO_2 = CH_3O + OH$
R71	$CH_3O + M = CH_2O + H + M$
R121	$H + C_2H_4(+M) = C_2H_5(+M)$
R572	$C_5 H_{10} - 1 + H = C_5 H_{11} - 1$
R763	$C_6H_5CH_3 = C_6H_5CH_2 + H$
R767	$C_6H_5CH_3 + H = C_6H_5CH_2 + H_2$
R769	$C_6H_5CH_3 + OH = C_6H_5CH_2 + H_2O$
R777	$C_6H_5CH_2 + HO_2 = C_6H_5CH_2O + OH$
R778	$C_6H_5CH_2 + OH = C_6H_5CH_2OH$
R779	$C_6H_5CHO + H = C_6H_5CH_2O$

 $C_6H_5CH_2O + OH (R777)$, leading to a net consumption of OH by toluene addition. As a result, reactions R767 and R769 become important radical sinks when toluene is added. This explains the observation in Figure 3 that the molar fraction of the radical pool decreases greatly with the toluene blending ratio. For the ignition of pure toluene/air (c = 1.0), the chain-initiation reaction to produce H radical is $C_6H_5CH_3 = C_6H_5CH_2 + H$ (R763) and its reaction rate is much smaller than the rates of the counterpart chain-initiation reactions $C_{10}H_{22} = H + C_{10}H_{21} - 5$ (R469), $C_5H_{11} - 1 = C_5H_{10} - 1 + H (R572)$, $C_7H_{15} - 1 = C_7H_{14}$ - 1 + H (R568), and $C_6H_{13} - 1 = C_6H_{12} - 1 + H (R570)$. Therefore, a significant decrease of H concentration is observed in Figure 3b for c = 1.0.

The chemical kinetics involved in toluene addition is further examined by suppressing toluene's chemical reactivity and keeping all other conditions unchanged (indicated here as 'inert toluene'). Figure 6 shows the temporal evolution of radical



Figure 6. Temporal development of radical pool (sum of CH₃, H, O, OH, and HO₂) during the homogeneous ignition of *n*-decane/toluene/ air mixtures with and without (equivalence ratio $\Phi = 1$) suppressing toluene's reactivity ($T_0 = 1400$ K, P = 1 atm).

pool for inert toluene and reactive toluene (i.e., the chemical reactivity of toluene is unchanged). The results are very close at the initial stage, implying that toluene-related reactions such as reaction R763 have little contribution to the initial radical buildup. However, as time goes on, significant difference between the radical pool growth of the inert toluene and that of the reactive toluene is observed. This indicates that the consumption of radicals due to toluene-related reactions (say, $C_6H_5CH_3 + H =$ $C_6H_5CH_2 + H_2$ and $C_6H_5CH_3 + OH = C_6H_5CH_2 + H_2O$ plays a vital role in the radical build-up. Moreover, such difference is amplified when the toluene blending ratio increases from c = 0.5to c = 0.9. This is mainly due to the facts that the production rates of radicals decrease with the reduction of *n*-decane and that the consumption rates of radicals increase with the amount of toluene in the mixture. Consequently, nonlinear behavior in the change of the ignition delay time with toluene blending ratio is observed in Figure 1.

Figure 1 also shows the ignition delay time with toluene's reactivity suppressed (inert toluene, dash-dotted line). The ignition delay time with 'inert toluene' is recorded when the heat release rate reaches its maximum. This is because at high level of inert toluene blending, the total amount of heat release is insufficient to increase the temperature by 400 K. The difference between the ignition delay time of reactive toluene and that of inert toluene demonstrates the pure kinetic effects of toluene addition on the ignition.

3.2. Nonpremixed Ignition Process. To assess the transport effects on *n*-decane ignition with toluene blending, the ignition of *n*-decane/toluene binary fuel blends by hot air is studied numerically in a counterflow configuration. All the simulations are conducted at the atmospheric pressure condition. Figure 7 shows the evolution of the temperature and OH mass



Figure 7. Evolution of the temperature and OH mass fraction distributions during the nonpremixed ignition in a counterflow configuration ($a = 50 \text{ s}^{-1}$, c = 0.5). The left and right vertical lines represent stagnation surfaces of the frozen flow and steady diffusion flame, respectively.

fraction distributions in the nonpremixed ignition process. It is seen that the ignition kernel first appears near the hot air side due to the exponential dependence of the reaction rate on the temperature. With the consumption of fuel, the ignition kernel then moves toward the fuel side. Eventually, the steady diffusion flame stays around the stoichiometric location. The left and right vertical lines represent the stagnation surfaces of frozen flow and steady diffusion flame, respectively. The ignition kernel and diffusion flame are shown to be always located on the hot air side of the stagnation surface. As a result, only through diffusion can the fuel molecules reach the reaction zone, and the nonpremixed ignition process is expected to be strongly affected by the fuel mass diffusivity. Unlike the fuel, the oxygen can easily get into the reaction zone through convection and diffusion.

Figure 8 plots the ignition delay time as a function of toluene blending ratio at different strain rates. The ignition delay time for



Figure 8. Ignition delay time as a function of toluene blending ratio in the nonpremixed counterflow and homogeneous configurations.

the homogeneous ignition process is also presented for comparison. The dashed line in Figure 8 represents results for the homogeneous ignition process diluted by nitrogen (the volumetric ratio between fuels and nitrogen is 1:9), which is in accordance with that of counterflow configuration. The nitrogen dilution is shown to have little effect on the homogeneous ignition delay time. Furthermore, it is observed that the ignition delay time of the nonpremixed ignition process in a counterflow configuration is much longer than that of the homogeneous configuration and strongly depends on the strain rate. This is due to the facts that there are heat and radical losses from the ignition kernel caused by transport in the counterflow configuration and that these losses are greatly affected by the strain rate. With the increase of the strain rate, the residence time of radicals in the ignition kernel decreases, and thereby, the radical pool becomes more difficult to be built up. Meanwhile, an increase of strain rate reduces the ignition kernel thickness and thus increases the gradients of temperature and radical mass fraction, which also promotes the heat and radical losses. Consequently, as shown in Figure 8, the ignition delay time for the nonpremixed ignition process increases greatly with the strain rate.

At low strain rates (say, $a = 20-100 \text{ s}^{-1}$ in Figure 8), the inhibitive effect of toluene addition on the nonpremixed ignition of *n*-decane by hot air is similar to that on the homogeneous ignition process. Again, two regimes are observed in the change of the ignition delay with the blending ratio: in the first regime, with a lower value of toluene blending ratio, τ is insensitive to change of *c* and the toluene addition has little effect on the ignition process; in the second regime, with the toluene dilution ratio above a certain value, τ increases exponentially with *c*. With the increase of the strain rate, the toluene blending ratio at the transition between these two regimes deceases. Therefore, the kinetic ignition inhibition caused by toluene addition becomes more pronounced at higher strain rate. At a high stain rate of a =400 s⁻¹, only the second regime is observed in Figure 8 and successful ignition cannot be achieved for $c \ge 0.6$.

The shifting of regime boundary can be explained by the transport nature of counterflow configuration. At high strain rates (say, $a = 400 \text{ s}^{-1}$), the characteristic flow residence time is

close to the characteristic chemical reaction time (i.e., $a^{-1} \sim \tau$). Under such conditions, the short flow residence time prevents the radical pool from being quickly built up and thereby the ignition process is very sensitive to kinetics. As a result, a small amount of toluene addition (which consumes the H and OH radicals through reactions R767 and R769) causes a rapid increase of the ignition delay time. On the other hand, at relative low strain rates (say, $a \leq 100 \text{ s}^{-1}$), the characteristic transport time is much longer than that of chemical reaction (i.e., $a^{-1} \gg \tau$). In such cases, the radical and heat losses caused by transport processes are less influential on the radical build-up. Consequently, toluene's ignition-inhibition effect on the nonpremixed ignition process is similar to that on the homogeneous ignition process, and the toluene blending ratio at the transition between two regimes remains nearly unchanged.

To further demonstrate the effects of strain rate and toluene blending on ignition, we plot in Figure 9 the temporal evolution



Figure 9. Temporal evolution of maximum H mass fraction during the nonpremixed ignition processes at different strain rates and toluene blending ratios.

of the maximum mass fraction of H radical during the unsteady nonpremixed ignition process. It is seen that, with the toluene addition (from c = 0.0 to c = 0.5), the ignition delay time increases, which is similar to the homogeneous case (see Figure 3b). However, the influence of toluene addition strongly depends on the strain rate: the high strain rate is shown to enhance the inhibitive effect of toluene addition on the accumulation of H radical. At t > 0.001 s, the difference between the maximum H mass fraction for c = 0.0 and that for c = 0.5 increases greatly when the strain rate is increased from $a = 20 \text{ s}^{-1}$ to $a = 400 \text{ s}^{-1}$. Therefore, the ignition inhibition by toluene addition to *n*decane depends on the kinetics as well as transport.

Usually the mixture fraction Z is introduced for the nonpremixed combustion. The overall reaction between elements C, H, and O can be assumed to be in the form of

$$\nu_{\rm C} \mathbf{C} + \nu_{\rm H} \mathbf{H} + \nu_{\rm O} \mathbf{O} \to \mathbf{P} \tag{5}$$

where $\nu_{\rm M}$ is the equivalent coefficient of element M. We employ the definition of mixture fraction proposed by Pitsch and Peters:³⁹

$$Z = \frac{\frac{Z_{\rm C}}{\nu_{\rm C}W_{\rm C}} + \frac{Z_{\rm H}}{\nu_{\rm H}W_{\rm H}} + 2\frac{Z_{\rm O,air} - Z_{\rm O}}{\nu_{\rm O}W_{\rm O}}}{\frac{Z_{\rm C,fuel}}{\nu_{\rm C}W_{\rm C}} + \frac{Z_{\rm H,fuel}}{\nu_{\rm H}W_{\rm H}} + 2\frac{Z_{\rm O,air}}{\nu_{\rm O}W_{\rm O}}}$$
(6)

where $W_{\rm M}$ and $Z_{\rm M}$ are molecular weight and mass fraction of element M, respectively. The subscripts air and fuel denote air and fuel jets, respectively.

Under the assumption of equal species diffusivities and unit Lewis number, the counterflow flame structure depends only on the mixture fraction and time. The governing equations in the Z-space are 40

$$\frac{\partial T}{\partial t} = \frac{1}{2} \chi \frac{\partial^2 T}{\partial Z^2} - \frac{\sum_{k=1}^N (h_k \omega_k W_k)}{\rho C_p}$$
(7)

$$\frac{\partial Y_k}{\partial t} = \frac{1}{2}\chi \frac{\partial^2 Y_k}{\partial Z^2} + \frac{\omega_k W_k}{\rho} \text{ for } k = 1, 2, ..., N$$
(8)

where χ is the scalar dissipation rate and it is defined as

$$\chi = 2D \left(\frac{\partial Z}{\partial x}\right)^2 \tag{9}$$

Here, *D* is the thermal diffusivity of the mixture (which is equal to the mass diffusivity under the assumption of unit Lewis number), and *x* is the axial space coordinate in the counterflow configuration. In the *Z*-space, eqs 7 and 8 indicate that the convective and diffusive transport of species and heat are controlled by the scalar dissipation rate χ .⁴⁰

Figure 10 shows the ignition delay time as a function of scalar dissipation rate χ_0 (defined at the stoichiometric location in the



Figure 10. Ignition delay time as a function of the inverse of scalar dissipation rate χ_0 (P = 1 atm).

initial frozen flow) for three toluene blending ratios. As expected, the ignition delay time is shown to decrease with the inverse of the scalar dissipation rate and to increase with the toluene blending ratio. Moreover, Figure 10 indicates that the ignition inhibitive effect caused by toluene addition becomes more pronounced at a higher scalar dissipation rate. This can be explained with the help of eqs 7 and 8. Unlike the homogeneous ignition process governed by eqs 1 and 2, the appearance of transport term inhibits the ignition, since the second order derivatives in eqs 7 and 8 are negative. There are two limits depending on the magnitudes of the transport term. On one limit, the transient term is negligible when the transport term is large enough to balance the source term, leading to a completely inhibition of ignition (the ignition delay time is infinitely long when the strain rate is close or above the extinction strain rate). On the other limit, there is a balance mainly between the transient and source terms while the transport term is relatively small and thereby negligible. Therefore, as indicated in Figure 10,

the increase of ignition delay time by toluene addition at a higher dissipation rate is always larger than that at a lower value of χ_0 .

To gain further understanding on the transport effects on the nonpremixed ignition process, we conduct sensitivity analysis with respect to the fuel mass diffusivity, thermal conductivity, and rates of two elementary reactions, $H + O_2 = O + OH (R1)$ and $C_6H_5CH_3 + H = C_6H_5CH_2 + H_2$ (R767). The sensitivity coefficient with respect to the elementary reaction rate is defined in eq 3. Similarly, the sensitivity coefficient of the ignition delay time with respect to the mass diffusivity of the k^{th} species is defined as

$$S_k = 10 \frac{\tau(1.1D_i) - \tau(D_i)}{\tau(D_i)}$$
(10)

where $\tau(1.1D_k)$ represents the ignition delay time when the mass diffusivity of the k^{th} species is artificially modified to be 1.1 times its original value (D_k) . The sensitivity coefficient with respect to the thermal conductivity is defined in the same way. According to the definition of eq 10, the larger the absolute value of S_k , the stronger the influence of the mass diffusion of the k^{th} species on the nonpremixed ignition process. Figure 11 shows the



Figure 11. Sensitivity coefficients of the nonpremixed ignition delay time with respect to the fuel mass diffusivity, thermal conductivity, and reaction rates of R1 and R767.

sensitivity coefficients at different strain rates ($a = 20 \text{ s}^{-1}$ and $a = 200 \text{ s}^{-1}$) and toluene blending ratios (c = 0.5 and c = 0.9). It is seen that the nonpremixed ignition delay time is very sensitive to the mass diffusivities of toluene and *n*-decane, while it is relatively insensitive to the mass diffusivity of oxygen. This is because the ignition kernel always stays on the hot air side of the stagnation surface (see Figure 7). As mentioned before, only through diffusion can the fuel molecules reach the ignition kernel, while the oxygen can easily get into the ignition kernel through diffusion as well as convection.

Artificially increasing the mass diffusivity of toluene or *n*-decane has two major influences on the ignition processes. On one hand, the local blending ratio of the specific fuel component in the ignition kernel increases due to its enhanced mobility. On the other hand, increasing the mass diffusivity of any fuel component helps the fuel mixture diffuse across the stagnation surface and into the ignition kernel, which facilitates the ignition. For *n*-decane, both influences enhance the ignition, and thus, the sensitivity coefficient of the ignition delay time with respect to the mass diffusivity of *n*-decane is always negative. For toluene, the first influence (which increases the local toluene blending ratio and thus inhibits the ignition) is dominated by the second influence (which increases the local equivalence ratio and thus facilitates the ignition). Therefore, the sensitivity coefficient with

respect to the mass diffusivity of toluene is also negative. As expected, Figure 11 shows that the absolute value of the sensitivity coefficient with respect to *n*-decane's mass diffusivity is much larger than that to toluene's mass diffusivity when these two fuel components are in the same amount (i.e., c = 0.5).

Figure 11 also shows that the sensitivity coefficient with respect to the fuel mass diffusivity and that to the rate of the key elementary reaction $(H + O_2 = O + OH)$ have the same order of magnitude. Therefore, the diffusion transport of fuel molecules plays a very important role in the nonpremixed ignition process. Furthermore, the sensitivity coefficient with respect to the thermal conductivity is shown to have a very large positive value. This reflects the significant inhibitive effect on the ignition process caused by heat conduction loss from the ignition kernel and reaction zone.

All the results discussed above are obtained at atmospheric pressure. In Figure 12 we plot the results at elevated pressures. It



Figure 12. Ignition delay time as a function of the inverse of scalar dissipation rate χ_0 at P = 1 atm and P = 10 atm. The toluene blending ratio is fixed to be c = 0.5.

is seen that the ignition delay time decreases as the pressure increases. Similar to the results at atmospheric pressure, at P = 10 atm, the ignition delay time decreases monotonically with the inverse of scalar dissipation rate and this can be explained with the help of eqs 7 and 8.

4. CONCLUSION

The premixed and nonpremixed ignition processes of n-decane/ toluene binary fuel blends with air at high temperature are investigated numerically considering detailed chemistry and transport. The main conclusions are as follows:

- 1. For the homogeneous (premixed) ignition, toluene addition is shown to prohibit the ignition process and two regimes are observed in the change of the ignition delay time with the toluene blending ratio. Sensitivity analysis and reaction path analysis for homogeneous ignition show that toluene's inhibitive effect on ignition is mainly attributed to reactions $C_6H_5CH_3 + H = C_6H_5CH_2 + H_2$ and $C_6H_5CH_3 + OH = C_6H_5CH_2 + H_2O$, which become important sinks of H and OH radicals.
- 2. For the nonpremixed ignition in the counterflow configuration, the ignition delay time is found to be strongly affected by the toluene blending ratio and strain rate. Due to the transport losses of radicals and heat from the ignition kernel (or reaction zone), the ignition delay time increases greatly with the strain rate. At a higher strain

rate with characteristic flow residence time close to the characteristic chemical reaction time, the ignition process is very sensitive to kinetics and thereby a small amount of toluene addition causes a rapid increase of the ignition delay time. Sensitivity analysis on the ignition delay time with respect to fuel mass diffusivity, thermal conductivity, and elementary reaction rates demonstrates that the diffusion transport of fuel molecules plays a very important role in the nonpremixed ignition process.

In this study, we have been focusing on ignition at hightemperature. The ignition at low-to-medium temperature is very important since the negative-temperature coefficient behavior occurs and strong chemistry-transport coupling might appear. This would be part of future work.

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Notes

The authors declare no competing financial interest.

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